



# Molten salt method of preparation and cathodic studies on layered-cathode materials $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ for Li-ion batteries

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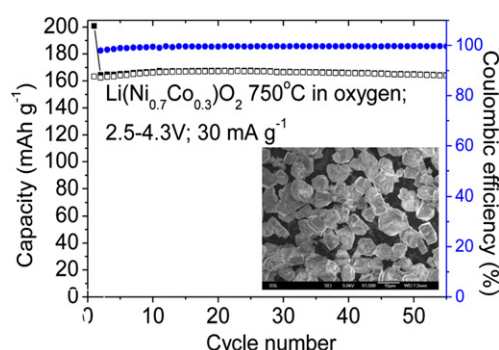
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## HIGHLIGHTS

- For the first time, we prepared layered  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  by molten salt method.
- Characterized by XRD, SEM, BET surface area techniques.
- The galvanostatic cycling studies of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  showed capacity value of 125 and 165  $\text{mAh g}^{-1}$  respectively, at 55th cycle and a current of 30  $\text{mA g}^{-1}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

Layered compounds,  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  (I) and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  (II) were prepared by molten salt method in temperature ranging from 650 to 950 °C. The effect of morphology, crystal structure and electrochemical properties of materials were evaluated by X-Ray Diffraction (XRD), Scanning Electron Microscopy and Brunauer-Emmett-Teller surface area, cyclic voltammetry (CV) and galvanostatic cycling. XRD pattern shows a hexagonal type structure with lattice parameters of  $a \sim 2.828 \text{ \AA}$ ,  $c \sim 14.096 \text{ \AA}$  for I and  $a \sim 2.851 \text{ \AA}$ ,  $c \sim 14.121 \text{ \AA}$  for II prepared in oxygen flow. The surface area of the compounds, I and II are 1.74 and 0.75  $\text{m}^2 \text{ g}^{-1}$  respectively. CV studies show a main anodic peak occur at  $\sim 3.8\text{--}3.94 \text{ V vs. Li}$  and a cathodic peak occur at  $\sim 3.6\text{--}3.7 \text{ V vs. Li}$ . Galvanostatic cycling studies are carried out at a current rate of 30  $\text{mA g}^{-1}$  in the voltage range of 2.5–4.3 V, at room temperature.  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at 750 °C in air show a reversible capacity of 145  $\text{mAh g}^{-1}$  at the 1st discharge cycle and 13% capacity fading between 2 and 56 cycles, whereas  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  reheated in the presence of oxygen deliver a high and stable reversible capacity of 165  $\text{mAh g}^{-1}$  at the end of 60th cycle.

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## 1. Introduction

Lithium cobalt oxide ( $\text{LiCoO}_2$ ) has been well studied [1,2] and used as a cathode material in the majority of commercial lithium ion batteries due to its excellent electrochemical properties, such as high operating voltage (4.0 V vs. Li), long life cycle, and easy

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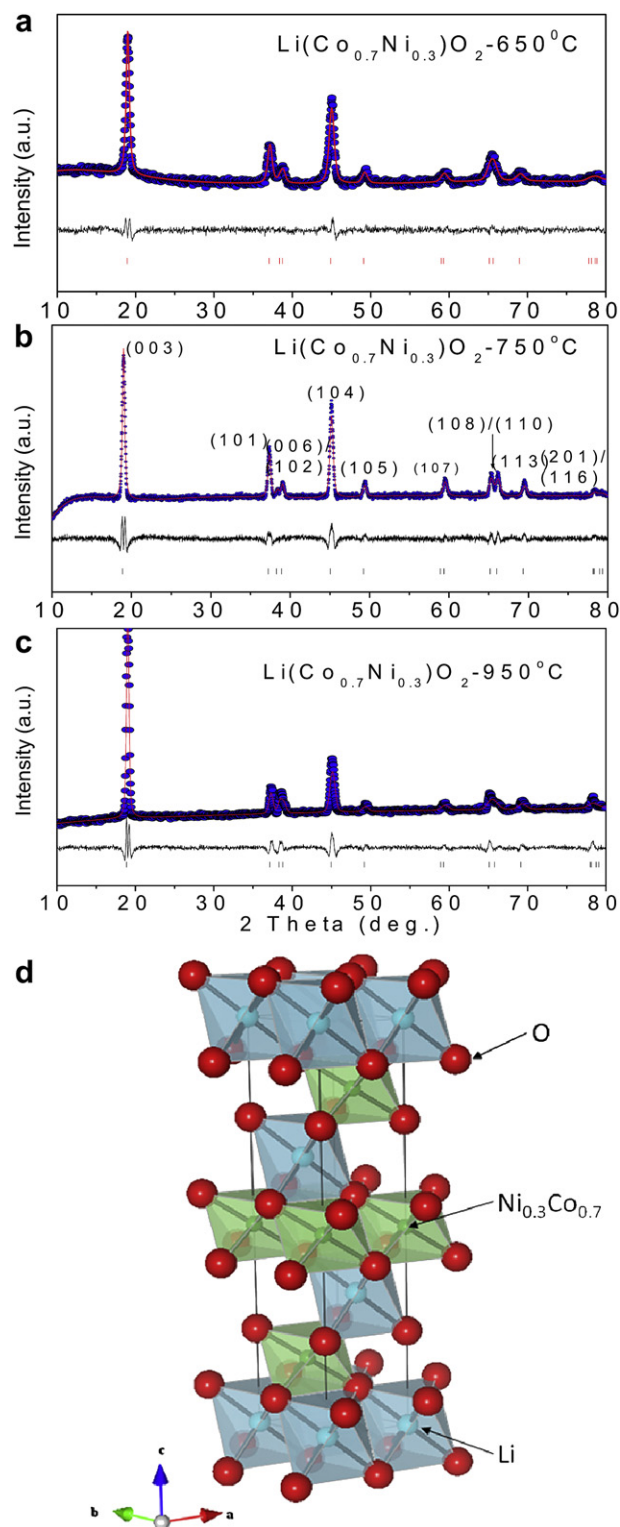
synthesis [1,2]. However, the high cost and toxicity of the above compound has triggered intensive researches on possible replaceable alternatives over the last few decades. Although  $\text{LiNiO}_2$  is one of the low cost cathode [1], it has drawbacks such as difficulties in preparing a stoichiometric phase and huge capacity fading during cycling is due to structural instability. In order to suppress or reduce the capacity fading, the group of Delmas, Ohzuku, Yamaki and others attempted the preparation and electrochemical studies on solid solutions of  $\text{Li}(\text{Ni}_{1-y}\text{Co}_y)\text{O}_2$  [3–10]. Later, various efforts have been made to reduce the cost and safety by partial substitution of Co with other low cost element like Ni, Mn, Ti, Fe, Al, Mg, Y [9–26] and surface coating [26–31]. Among  $\text{Li}(\text{Ni}_{1-y}\text{Co}_y)\text{O}_2$  ( $x = 0.1–0.8$ ) solid solutions,  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  are one of the best attractive material in terms of cost and capacity [6].

In this project, we attempted to reduce cobalt content by substituting partially or fully with Ni element. Lithium nickel-cobalt oxides phases,  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  with the hexagonal layer structure are being investigated as prospective second-generation  $\sim 4\text{V}$ -cathode (positive electrode) materials. These oxides contribute to the reversible cathodic capacity through both  $\text{Ni}^{3+/4+}$  and  $\text{Co}^{3+/4+}$  redox couples. The  $\text{Ni}^{3+}$  ions are trivalent and play a beneficial role by ways of stabilizing the layer structure and ensuring good electronic conductivity. In literature above,  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  are prepared by solid state [32], sol–gel [33], freeze drying [34], mixed hydroxide or co-precipitation method [35], combustion method [33] and spray drying [36]. The compound,  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  was previously prepared by solid state [37] and Sol–gel method [23]. Previously one pot molten salt synthesis method used for the preparation of layered cathodes namely,  $\text{LiCoO}_2$  [38],  $\text{Li}(\text{Co}_{1-x}\text{Al}_x)\text{O}_2$  [39],  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  [40], and  $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.4}\text{Al}_{0.1})\text{O}_2$  [41] using  $0.88\text{M LiNO}_3:0.12\text{M LiCl}$  salt and  $\text{LiMn}_2\text{O}_4$  using  $0.5\text{M NaCl}:0.5\text{M KCl}$  salt [42]. In addition to above cathode materials few other simple binary oxide, ( $\text{TiO}_2$ ) [43,44] and ternary oxides, ( $\text{MCo}_2\text{O}_4$ ,  $\text{M} = \text{Co}, \text{Zn}, \text{Cu}$ ) [45–47] anode materials were prepared by molten salt method. For academic interest, presently, we extended the preparation of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  by molten salt method at  $650–950^\circ\text{C}$  for 6 h in air. They were characterized by wide variety of techniques and their cathodic properties vs. Li-metal were examined.

## 2. Experimental

The molten salt method (MSM) involved mixing  $\text{LiNO}_3$  (Alfa Aesar),  $\text{LiCl}$  (Merck) salts in the mole ratio 0.88:0.12 (eutectic composition) and metal salts,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99%),  $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  (Merck, 99%) corresponding to the mole ratio, (0.3:0.7) and (0.7:0.3). The total mole ratio of Ni and Co-salts: eutectic mixtures were kept at 1: 10. All reactants were put in an alumina crucible, heated in air to  $650–950^\circ\text{C}$  at a rate of  $3^\circ\text{C min}^{-1}$  and kept for 3 h in air. After cooling down to room temperature, the obtained product was thoroughly washed with de-ionized water, decanted several times to remove excess lithium salts and filtered. The final product was dried in an air oven at  $80^\circ\text{C}$  for 24 h, after which an amount of black powder was obtained. Previous many literature studies of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared by solid state method showed that oxygen was needed to maintain the proper oxidation state of Ni. Our final MSM powder prepared at  $750^\circ\text{C}$  in air was further heated at  $750^\circ\text{C}$  in the presence of flowing oxygen for 12 h in a tubular furnace (Carbolite, UK). We note for large scale synthesis disadvantages like lithium abundance will be an important limitation for the deployment of lithium batteries in electric vehicles, the present synthetic method presented is only interesting from a basic point of view.

The powder X-ray diffraction (XRD) patterns were taken using Empyrean X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. Rietveld refinement of XRD data was carried using TOPAS-R (version 2.1) software. The morphology and surface area of powders were



**Fig. 1.** X-ray diffraction patterns of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  powders prepared at a temperatures, (a)  $650^\circ\text{C}$ , (b)  $750^\circ\text{C}$  and (c)  $950^\circ\text{C}$ . Symbols and continuous lines represent experimental and fitted (Rietveld refined) X-ray diffraction patterns. The difference patterns are also shown. Vertical bars represent the positions of allowed (hkl) lines. (d) General crystallographic representation of layered compound,  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ .

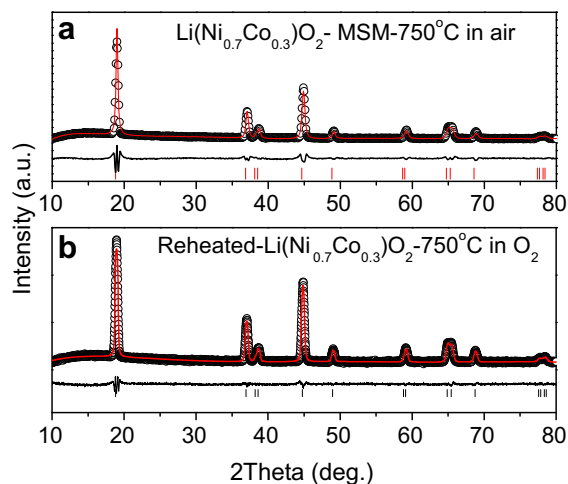
examined by scanning electron microscope (SEM) (JEOL JSM-6700F) and Brunauer, Emmett and Teller (BET) (Micromeritics Tristar 3000 (USA)) techniques. For cathodic studies, the electrodes were fabricated with active material, super P carbon black and binder (Kynar 2801) in the weight ratio 70:15:15. They were mixed using N-methyl pyrrolidone (NMP) as solvent to dissolve the binder. The slurry was then coated on to an etched aluminum foil (15  $\mu\text{m}$  thick; Alpha Industries, Japan) to get thick film (15  $\mu\text{m}$ ) using the doctor blade technique. The film was then dried in a vacuum oven at 80  $^{\circ}\text{C}$ , pressed between twin stainless steel rollers and cut into 16 mm diameter circular disks (geometrical area of the electrode was 2.0  $\text{cm}^2$  and weight of active material was  $\sim 6$  mg). Coin-type cells (size, 2016) were assembled using this composite electrode as cathode in an Ar-filled glove box (MBrann, Germany). Lithium metal foil (Kyokuto metal Co., Japan) was used as the anode electrode (negative). 1M  $\text{LiPF}_6$  in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 V/V) (Merck) was the electrolyte and glass fiber membrane was used as the separator. Charge–discharge cycling at constant current and cyclic voltammetry were carried out on the cells by using multi channel Bitrode multiple battery tester (Model SCN, Bitrode, USA) and Mac-pile II, system (Bio-logic, France). The cells were aged for 8 h before the tests and all studies were carried out at ambient temperature ( $\text{RT} = 24$   $^{\circ}\text{C}$ ).

### 3. Results and discussion

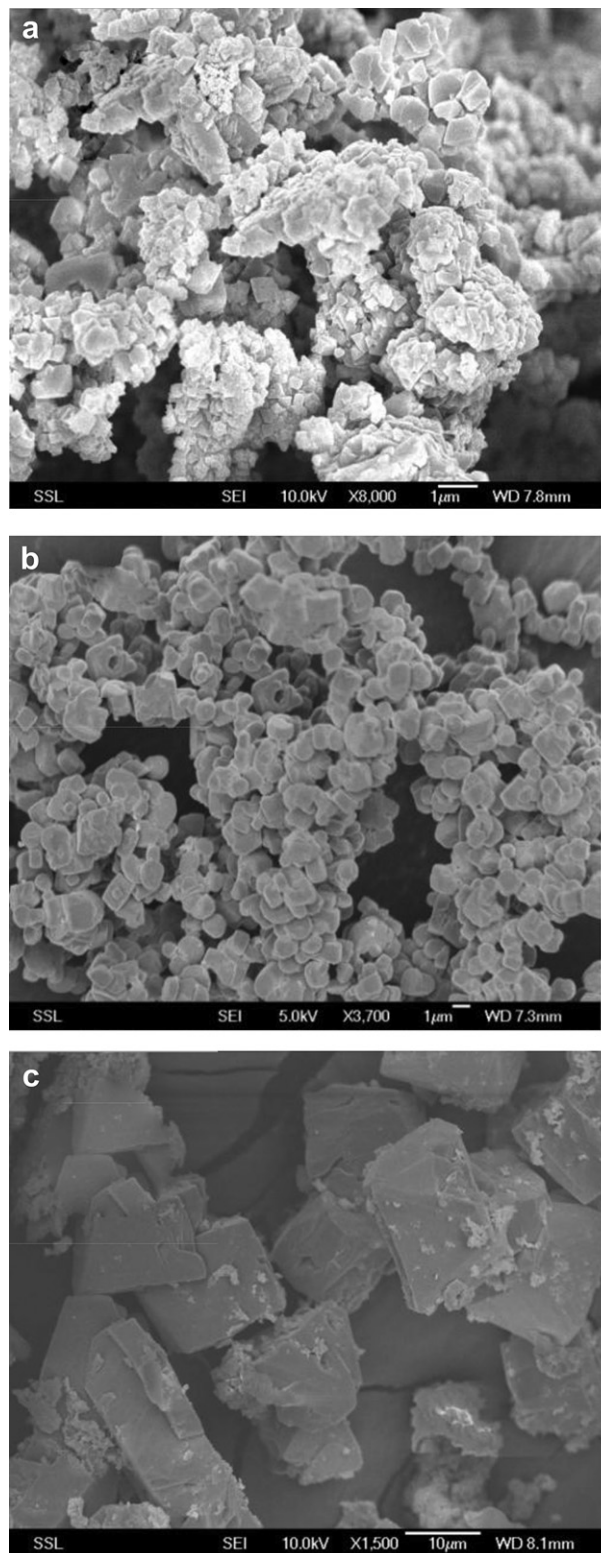
#### 3.1. Structure and morphology

The prepared compounds are black crystalline powders. The Rietveld refined XRD patterns of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  compounds are shown in Figs. 1 and 2. They were indexed on the basis of hexagonal layered  $\text{LiCoO}_2$  type structure. The Rietveld refinement was carried out assuming the space group  $R\bar{d}3m$  with  $\alpha$ - $\text{NaFeO}_2$  type structure, transition metal ions (Co, Ni) occupy at 3a site (0,0,0), Li at the 3b site (0,0,  $\frac{1}{2}$ ), and O at the 6c site (0,0,z). Refined lattice parameter values of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  are: 650  $^{\circ}\text{C}$ :  $a = 2.843(4)\text{\AA}$ ,  $c = 14.079(2)\text{\AA}$ ,  $c/a = 4.95$ ,  $z = 0.259$ ; 750  $^{\circ}\text{C}$ :  $a = 2.828(3)\text{\AA}$ ,  $c = 14.096(2)\text{\AA}$ ,  $c/a = 4.98$ ,  $z = 0.271$ ; and 950  $^{\circ}\text{C}$ :  $a = 2.839(7)\text{\AA}$ ,  $c = 14.129(5)\text{\AA}$ ,  $c/a = 4.97$ ,  $z = 0.262$ . The compound,  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at 750  $^{\circ}\text{C}$  shows a nice  $c/a$  ratio of 4.98 and well-defined splitting of the XRD lines assigned to the pairs of

Miller indices (hkl), (006,102) and (108,110) at 2 theta around 37 and 65 are good indication of a well-ordered layer structure (Fig. 1b), whereas a disordered type structure was noted for the sample prepared at 650  $^{\circ}\text{C}$  (Fig. 1a). The lattice parameter values of



**Fig. 2.** X-ray diffraction patterns of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared by MSM (a) 750  $^{\circ}\text{C}$  in air, (b) reheated at 750  $^{\circ}\text{C}$  in oxygen for 12 h. Symbols and continuous lines represent experimental and fitted (Rietveld refined) X-ray diffraction patterns. The difference pattern is also shown. Vertical bars represent the positions of allowed hkl lines, CuK $\alpha$  radiation was used to record the XRD patterns.



**Fig. 3.** Scanning electron microscopy (SEM) images of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at (a) 650  $^{\circ}\text{C}$ , scale bar: 1  $\mu\text{m}$  (b) 750  $^{\circ}\text{C}$ , scale bar: 1  $\mu\text{m}$  and (c) 950  $^{\circ}\text{C}$ , scale bar: 10  $\mu\text{m}$ .

$\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared at 750 °C, in air are  $a = 2.856(6)\text{Å}$ ,  $c = 14.152(4)\text{Å}$ ,  $c/a = 4.95$ ,  $z = 0.260$  and reheated sample in presence of oxygen are  $a = 2.851(1)\text{Å}$ ,  $c = 14.121(2)\text{Å}$ ,  $c/a = 4.95$ ,  $z = 0.256$ .

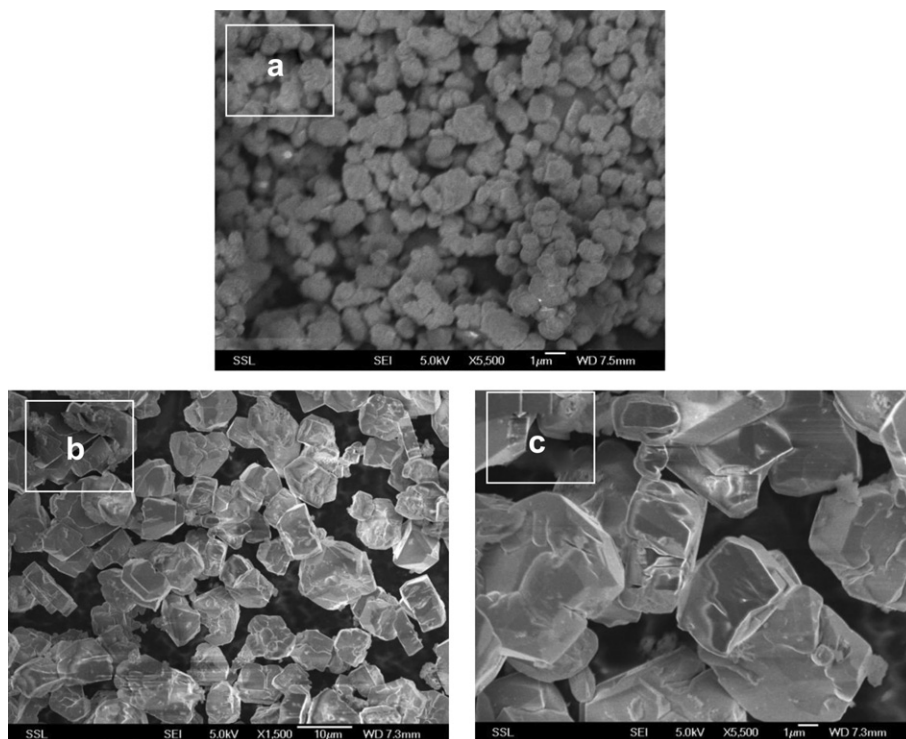
A slight differences in  $a$  and  $c$  values of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  were noted depending on preparation method for example solid method:  $a = 2.85\text{ Å}$ ,  $c = 14.25\text{ Å}$  [8],  $a = 2.859\text{ Å}$ ,  $c = 14.155\text{ Å}$ , Zoxy: 0.259 [6],  $a = 2.868\text{ Å}$ ,  $c = 14.10\text{ Å}$  [17], free drying method:  $a = 2.855\text{ Å}$ ,  $c = 14.15\text{ Å}$  [34], combustion method at 800 °C in air  $a = 2.8565(1)\text{ Å}$  and  $c = 14.1576(5)\text{ Å}$ , Zoxy: 0.258 [48]. The lattice parameter values of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  are similar to reported literature ( $a = 2.799\text{ Å}$ ,  $c = 14.15\text{ Å}$ ) [11]. The observed lattice parameters of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  are lower than that of  $\text{LiNiO}_2$  prepared solid state method ( $a = 2.881\text{ Å}$ ,  $c = 14.19\text{ Å}$ ) [32], single source precursor method ( $a = 2.877(5)\text{ Å}$  and  $c = 14.201(4)\text{ Å}$ ) [49] and higher than that of the MSM  $\text{LiCoO}_2$ -750 °C in air ( $a = 2.818\text{ Å}$  and  $c = 14.056\text{ Å}$ ) [38] and MSM  $\text{Li}(\text{Co}_{0.5}\text{Ni}_{0.5})\text{O}_2$ -750 °C in air ( $a = 2.8398\text{ Å}$  and  $c = 14.094\text{ Å}$ ) [41] and close to  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$  ( $a = 2.867\text{ Å}$  and  $c = 14.17\text{ Å}$ ) [29]. The lattice parameter values differs depending on the composition of Ni and Co, which are due to differences in the ionic radii of  $\text{Co}^{3+}$  (0.53 Å) and  $\text{Ni}^{3+}$  (0.56 Å) [32].

The SEM photographs of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at temperatures 650, 750 and 950 °C are shown in Fig. 3a–c, as expected, increase in particle size with temperature was noted, indicating agglomeration of submicron particles with platelet like morphology for all temperatures. The size of the agglomerates ranged from 2 to 4 μm. The SEM images of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  showed that the two types of samples have differences in size. The one without oxygen (Fig. 4a) has a smaller size (ranged from 1 to 2 μm) while the sample upon oxygen treatment (Fig. 4b) has a much larger size (5–10 μm), was flatter with a more crystal-like surface. The size and surface of the agglomerates affect the performance of the battery greatly, which will be discussed in the later section. The BET surface areas of select samples of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and

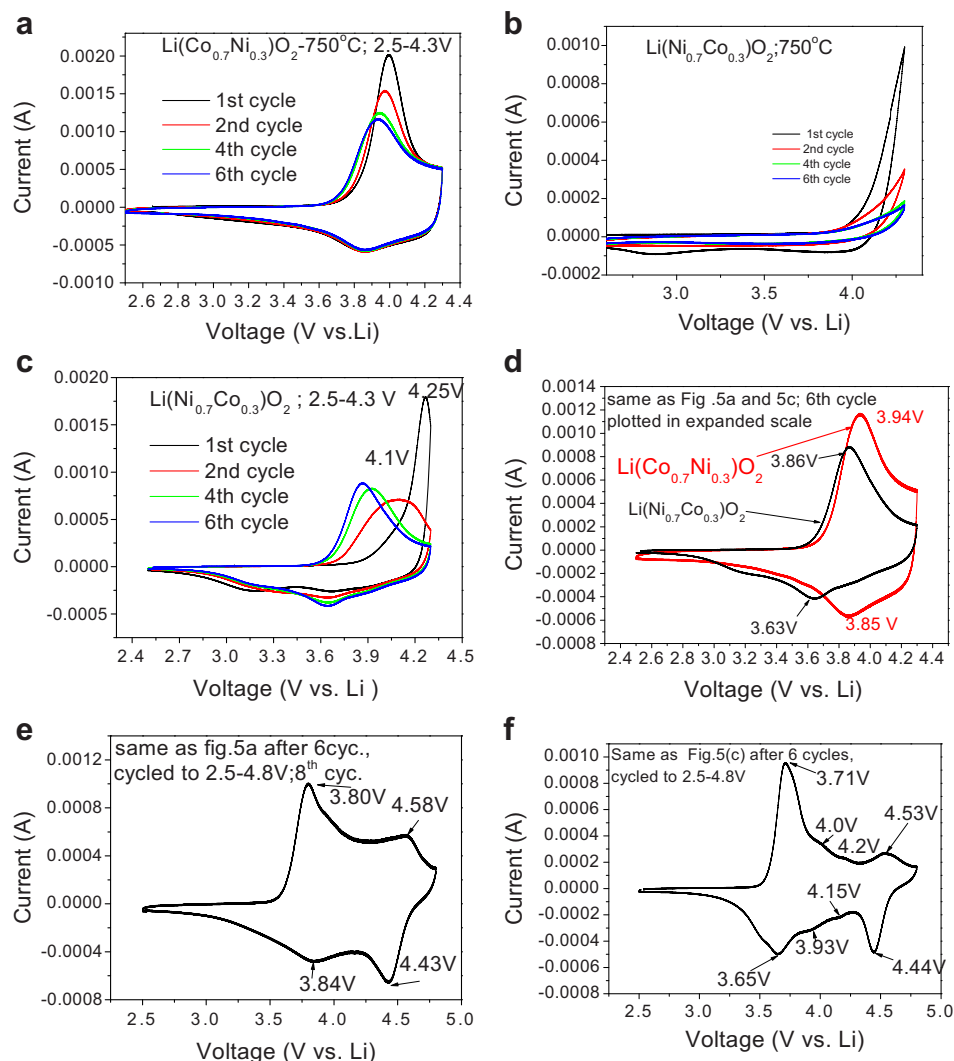
$\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  reheated in oxygen are 1.74 and 0.74 ( $\pm 0.1$ )  $\text{m}^2\text{ g}^{-1}$ , respectively, for compounds prepared at 750 °C.

### 3.2. Cyclic voltammetry

The cyclic voltammograms (CV) of the cells with Li metal as the counter and reference electrode were recorded at ambient temperature (RT = 25 °C), in the range 2.5–4.3 V vs.  $\text{Li/Li}^+$ , up to 5 cycles. The CVs, carried out at a fairly low scan rate of 0.058  $\text{mV s}^{-1}$  for  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  are shown in Fig. 5. In the case of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ -750 °C (Fig. 5a), the first-cycle anodic peak (extraction of Li ions from the lattice) occurs at 4.0 V (vs. Li) whereas the main cathodic (insertion of Li) peak is at  $\sim 3.68$  V. In the second cycle, the anodic peak shifts to a lower voltage, but the corresponding cathodic peak does not show any shift, whereas differences first and second subsequent cycles peak voltages are clearly seen in with  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  (Fig. 5c). The shift in the anodic peak voltage is an indication of the 'formation' of the electrode in the first few-cycles, whereby the active material makes good electrical contact with the conducting carbon particles in the composite electrode, the Al-substrate and the liquid electrolyte. Similar formation behavior was noted other cathode like  $\text{LiVPO}_4\text{F}$  [50]. The hysteresis ( $\Delta V$  = the difference between the anodic and cathodic main peak voltages) at the end of 6th cycle (Fig. 5c) is 0.10 V, indicating just reversibility (or quasi reversible) of the charge–discharge reaction. In addition, anodic and cathodic peak voltages at 4.58 and 4.43 V vs. Li when cycling up to 4.8V (Fig. 5e) are due to hexagonal phase transformations of  $\text{LiCoO}_2$  phases [49,51–53]. The anodic and cathodic peaks of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ -750 °C (Fig. 5b,c) are slightly different from  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  (Fig. 5a). The minor peaks in the CV are due to hexagonal phase transitions of  $\text{LiNiO}_2$  [49,54–57]. The main anodic/cathodic peak voltages are shifted to lower voltage value (Fig. 5d) and the CVs of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared in air (Fig. 5b) showed no well-defined peak potentials



**Fig. 4.** Scanning electron microscopy (SEM) images of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared at (a) 750 °C in air, scale bar: 1 μm, (b,c) reheated the sample (a) at 750 °C, 12 h in oxygen, scale bars: 10 and 1 μm.



**Fig. 5.** Cyclic voltammograms (*i*–*V* curves) of (a)  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ -750 °C in air, (b)  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ -750 °C in air, (c) reheated  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ -750 °C in oxygen flow, (d) for clarity 6th CVs of Fig. 5a, c are shown in expanded scale, note that peak currents are not normalized with active mass, (e) same as Fig. 5a after 6th cycle cycled in the range, 2.5–4.8 V; 8th cycle are shown and (f) same as Fig. 5c after 6th cycle cycled in the range, 2.5–4.8 V; 8th cycle are shown, scan rate, 0.058  $\text{mV s}^{-1}$ , at ambient temperature (RT), figures (a–d) cycled in the voltage range, 2.5–4.3 V.

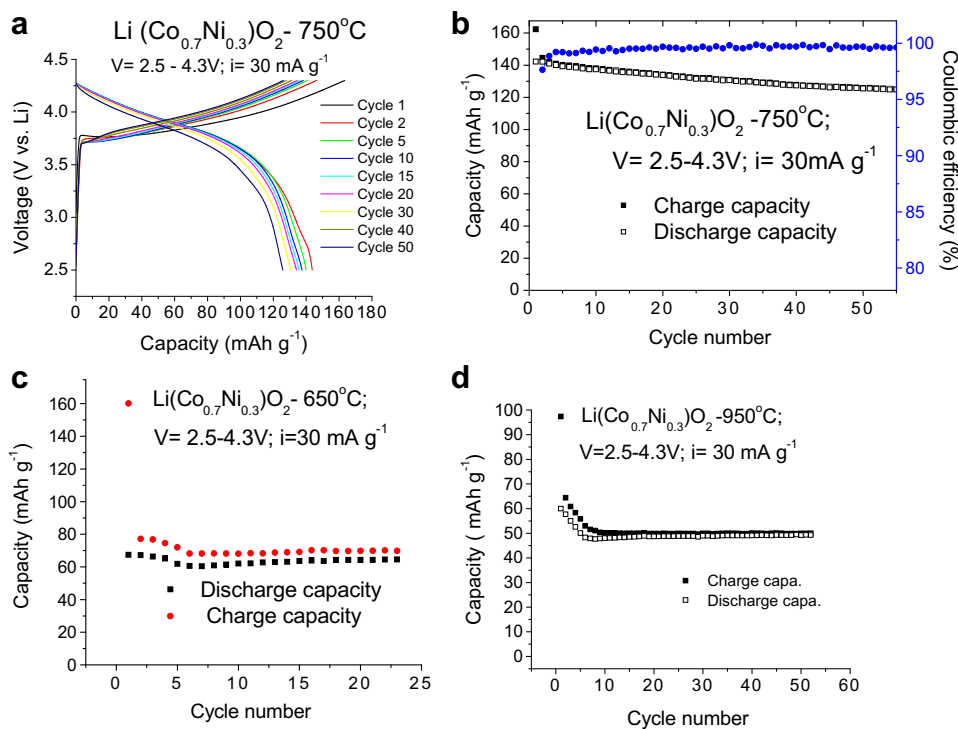
of layered oxides, which is clearly reflected in the cycling performance.

The anodic/cathodic peaks observed in the voltage region, 3.60–3.94 V in  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  can be attributed to redox couple,  $\text{Ni}^{3+/4+}$  and  $\text{Co}^{3+/4+}$ . A slight difference in the redox couple are seen with respect to composition of the samples. This is due to interactions between the metal ions within the layers in the structure, the redox voltages can either be shifted considerably from that encountered in the un-doped compound,  $\text{LiNiO}_2$  or  $\text{LiCoO}_2$  or may be identical for both  $\text{Ni}^{2+/3+}$  and  $\text{Ni}^{3+/4+}$  in the mixed oxide system.

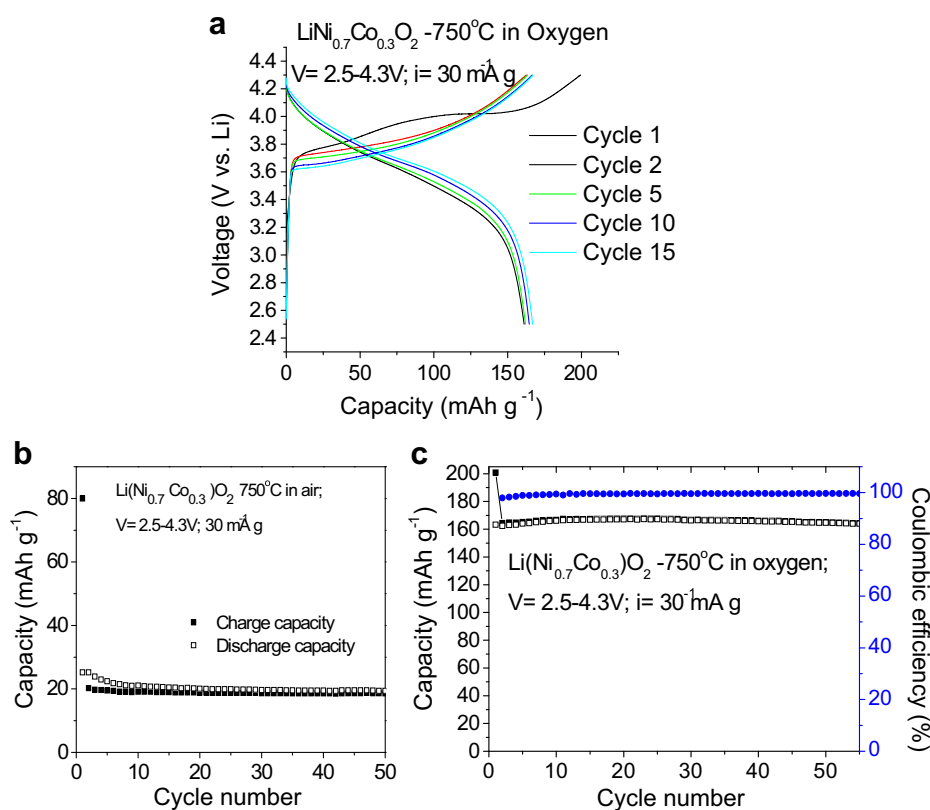
### 3.3. Charge discharge cycling

Galvanostatic charge–discharge cycling of cells with  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at 750 °C are shown in Fig. 6a. Cycling was carried out at a current rate (*i*) of 30  $\text{mA g}^{-1}$  at ambient temperature up to 55 cycles in the voltage window of 2.5–4.3 V vs. Li. The capacity vs. cycle number plots for all the compounds are shown in Fig. 6b. The open circuit voltage (OCV) of the fabricated and aged overnight cell are ~2.8 V. Passage of current during the first-charge

cycle caused a sudden increase of cell voltage, for all temperature, to ~3.8–3.9 V, followed by a flat voltage profile up to a capacity of 5  $\text{mAh g}^{-1}$ . Afterwards, the cell voltage gradually increased to the cut-off value. The first-discharge and subsequent charge–discharge curves are smoothly varying curves, typical of the single-phase Li-de-intercalation/intercalation reaction. The first-charge capacity of the sample is 165  $\text{mAh g}^{-1}$  (0.60 moles Li per mole of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ ). The observed irreversible capacity (ICL) of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ -750 °C between the first-discharge and first-charge cycle was 20  $\text{mAh g}^{-1}$ . The observed de-intercalation/intercalation mechanism of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  was similar to previous original work reported by Delmas group [3,7]. The capacity vs. cycle number plots (Fig. 6b) and cycling profiles of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ -750 °C shows a reversible capacity of 135 and 126 ( $\pm 3$ )  $\text{mAh g}^{-1}$  at the end of 20th and 50th cycle, and about 6 and 13% capacity fade was noted between 2nd to 20th or 55th cycle, respectively (Fig. 6b). Sol–gel prepared compound showed a reversible capacity value of 133  $\text{mAh g}^{-1}$  with 8% capacity fading between 2 and 20 cycles at a current rate of 0.1C [23]. The samples, prepared at 650 °C and 950 °C, showed a reversible capacities of 60 and 50  $\text{mAh g}^{-1}$ , respectively at the end of 20th or 50th cycle (Fig. 6c,d). The



**Fig. 6.** (a) Galvanostatic cycling curves of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  prepared at 750 °C in air, (b) Capacity vs. cycle number plots of (a), (c) 650 °C and (d) 950 °C. Voltage range, 2.5–4.3 V and current rate (i) of 30 mA g<sup>-1</sup>.



**Fig. 7.** (a) Galvanostatic cycling curves of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared at 750 °C in presence of oxygen, (b) Capacity vs. cycle number plots of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared at 750 °C in air and (c) reheated sample at 750 °C in oxygen. Voltage range, 2.5–4.3 V and current rate (i) of 30 mA g<sup>-1</sup>.

coulombic efficiency at end of 15th cycle for 650 °C, 750 °C and 950 °C are 95, 98.5, 99%, respectively. The observed differences in the cycling behavior of  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  are due to the variations in the crystallinity is due to reaction temperature, morphology and disorder in the crystal structure which are known to govern the cathodic properties. Further improvement in the capacity retention is possible by optimizing the synthesis conditions using molten salt-routes through proper selection of molten salts.

Charge–discharge cycling studies of reheated  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  in presence of oxygen are shown in Fig. 7a at a current density of  $30 \text{ mA g}^{-1}$  with the voltage range from 2.5 to 4.3 V vs. Li. Selected voltage–capacity profiles are shown in Fig. 7a and the capacity vs. cycle numbers plots of the sample prepared  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ -750 °C in air and oxygen are shown in Fig. 7b and c. As seen from of CV studies (Fig. 5b) and charge–discharge cycling (figures not shown) sample prepared in air showed not well defined characteristic electrochemical cycling profiles. Charge–discharge profiles show a low capacity of about  $21 \text{ mAh g}^{-1}$  and in addition, it was noted that the redox peaks were not well defined for the sample prepared in absence of oxygen. In contrast, the graphs of the cell prepared with oxygen show high and stable capacity of  $165 \text{ mAh g}^{-1}$  ( $0.60 \text{ mol Li}$  per mole of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ ) at the end of the 60th cycle and almost nil capacity fading was noted during cycling. The observed irreversible capacity loss during 1st charge–discharge cycle was  $40 \text{ mAh g}^{-1}$  and our ICL value was close to previous report on  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ . The coulombic efficiency was about 98% after 25 cycles (Fig. 7c). The present studies show that irrespective of oxidizing flux ( $\text{LiNO}_3$ ) used in molten salt synthesis, second heat treatment in presence of flowing oxygen is needed during preparation of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  to deliver high and stable cathodic performance.

Present observed capacity values are better than that of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  prepared by solid state method [17] and solution method [17], they reported reversible capacity of at end of 50th cycle are 128 and  $98 \text{ mAh g}^{-1}$  at current rate of 0.1C with a capacity retention value (1–50 cyc.) of 76 and 70%, respectively [17], and 72% capacity retention (1–50cyc.) with freeze-drying method [34]. Urea combustion method [38] compound showed a reversible capacity of  $\sim 135 \text{ mAh g}^{-1}$  with 84% capacity retention at the end of 40th cycle, when cycled in the range, 2.5–4.4 V. Sol–gel [58] prepared  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  showed 74% capacity retention at the end of 50th cycle, at a current rate of 0.1C, the voltage range, 3.0–4.3 V vs. Li. It clearly indicates present compound show almost nil capacity fading (Fig. 7c) with a good capacity value of  $165 \text{ mAh g}^{-1}$  at end of 60th cycle.

#### 4. Conclusions

The compounds  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  with the layer structure were prepared using molten salt method. The materials were characterized by powder XRD, SEM, BET method and their cathodic electrochemical behavior in cells with Li-metal as counter electrode were tested. Cyclic voltammograms of above compounds showed redox processes occur at 3.6–3.94 V vs. Li, which corresponds to the  $\text{Ni}^{3+/4+}$  and  $\text{Co}^{3+/4+}$  redox couple, and slightly lower average operating potential was noted for  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ . Galvanostatic charge–discharge cycling was carried out at  $30 \text{ mA g}^{-1}$ , with voltage range, 2.5–4.3 V. The compound,  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$ -750 °C prepared under oxygen showed a high and stable capacity of  $165 \text{ mAh g}^{-1}$  at the end of the 60th cycle, and  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$ -750 °C showed reversible capacity of  $125 \text{ mAh g}^{-1}$  at the end of the 55th cycle with 13% capacity fading between 2nd and 55th cycle. The observed capacity and retention value of  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  was better than the other preparation methods reported in literature. Further

detail structural studies on  $\text{Li}(\text{Ni}_{0.7}\text{Co}_{0.3})\text{O}_2$  and  $\text{Li}(\text{Co}_{0.7}\text{Ni}_{0.3})\text{O}_2$  compounds using neutron diffraction studies are in progress.

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